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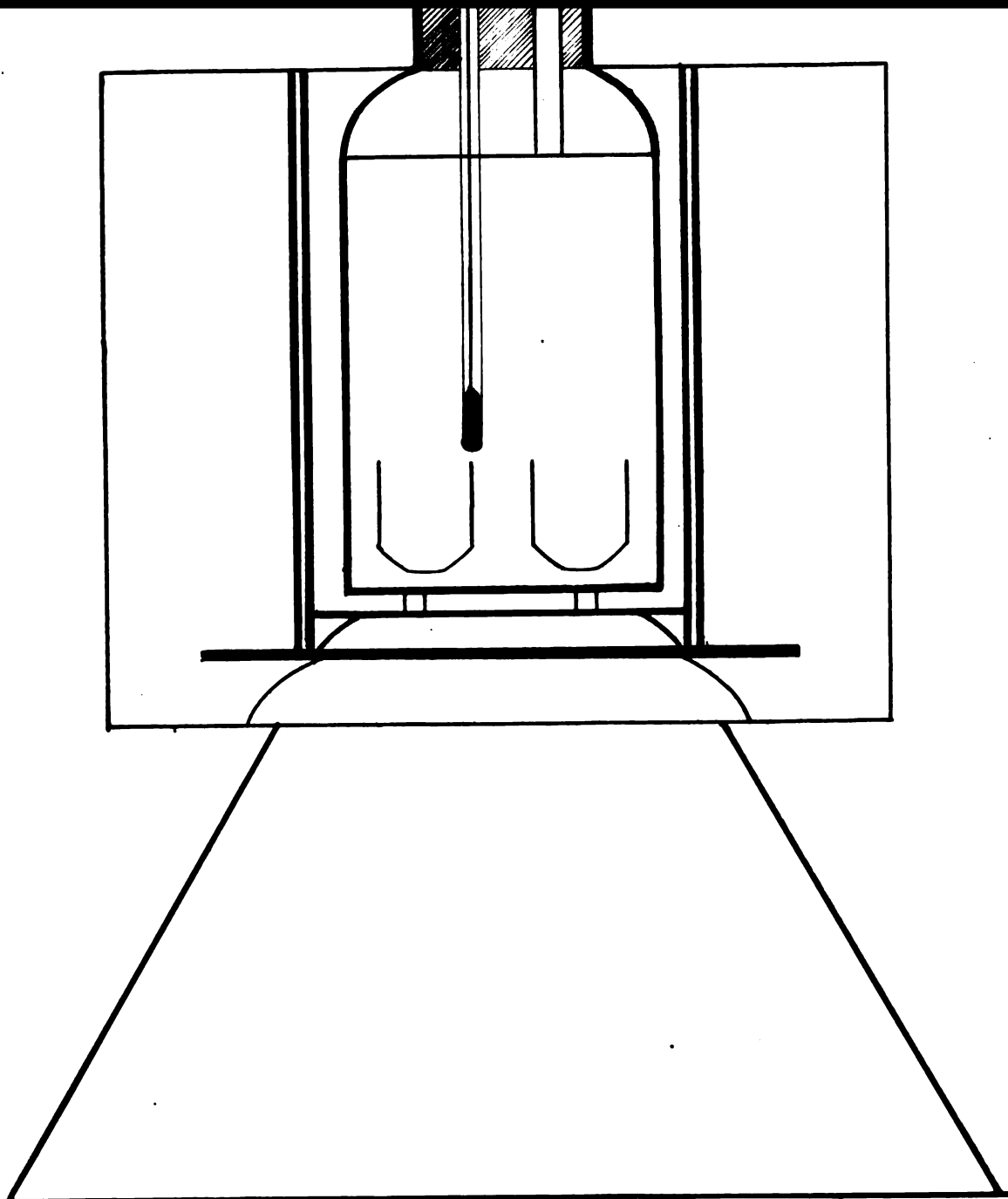
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The Volatility of Chromium Trioxide

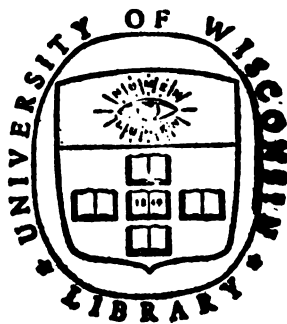
Raymond C Benner

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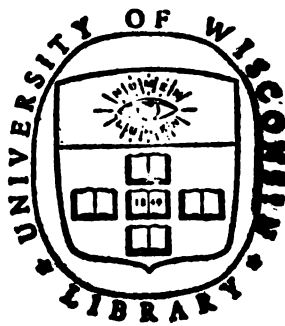
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THE VOLATILITY OF CHROMIUM TRIOXIDE

by

RAYMOND CALVIN DENNER

A Thesis Submitted for the Degree of
MASTER OF ~~SCIENCE~~ *PHIL.*

UNIVERSITY OF WISCONSIN

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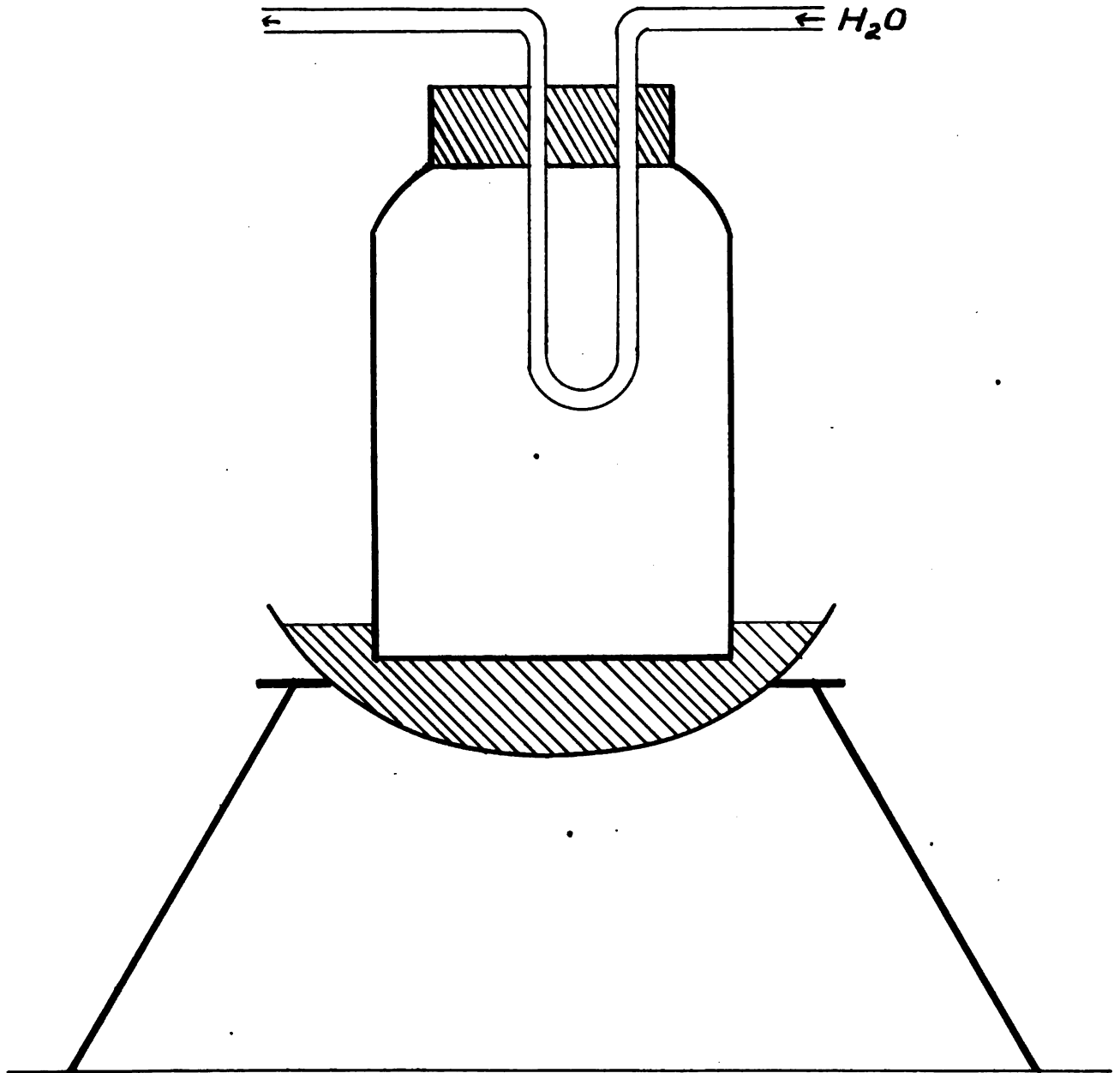
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C O N T E N T S .

- I Introduction and work of Arctowski.
- II General phenomena attending volatilization.
- III Detection of moisture and other impurities.
- IV Effect of water on the volatilization of chromium trioxide.
- V Effect of temperature on the volatilization.
- VI Effect of diminution of pressure on the volatilization.
- VII Effect of the amount of surface on the volatilization.
- VIII The fractionation of CrO_3 by revolatilization.
- IX Effect of oxygen and carbon dioxide on the percentage volatilized.
- X Conclusions.

Fig. 1.



Arctowski observed that when CrO_3 was heated, red vapors were evolved (1) and concludes that the red vapors may be chromium trioxide carried off mechanically by the oxygen liberated during decomposition, a true volatilization, or both combined. To determine if it were possible to volatilize chromium trioxide, he put the oxide, from which all water had been removed with the greatest possible care, in a bottle (Fig. 1) placed in an oil bath. A "U" tube was introduced through the cork and was cooled by a stream of water, as this offers a cool surface on which the oxide can condense. The air was exhausted to 16 mm. and after exhausting, the temperature was raised to $110^\circ - 130^\circ$, where it was kept for 20 hours, when small red needle-like crystals were observed on the end of the "U" tube. If the heating were continued for four days at a temperature of 125° and a pressure of 16 mm., it is possible to obtain crystals of the sublimed oxide 2 mm. in length, and by obtaining these crystals of sublimed oxide so far below the melting point of the oxide (193°), proves that it is possible to sublime the oxide without decomposition.

When pure chromium trioxide is heated it assumes a much darker color than its usual deep red, and considerably

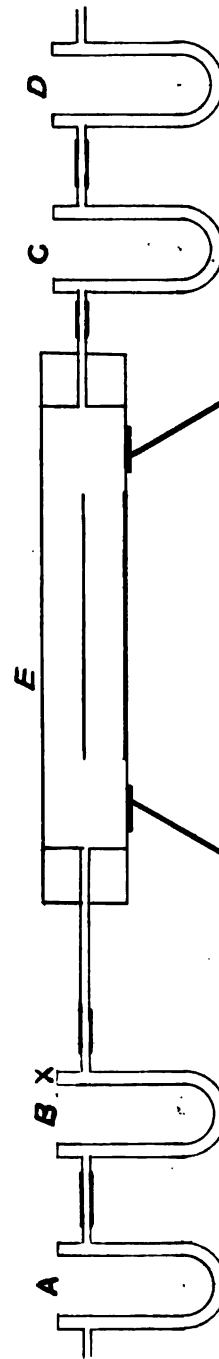
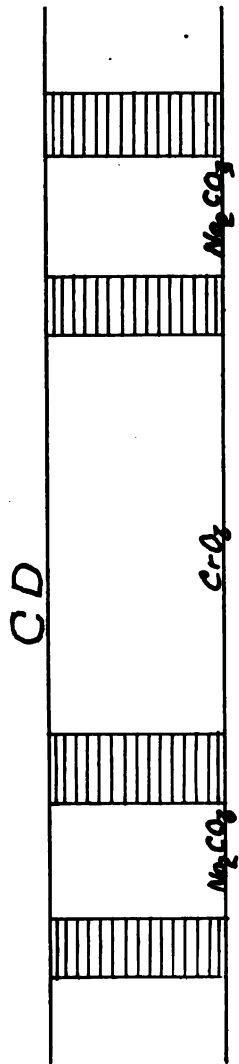
(1) Zeit. Anorgan. Chem., 9, 29.

below its melting point becomes nearly black, resembling potassium permanganate in color. The trioxide melts at 193° ; and above this temperature oxygen is evolved, the sesquioxide being formed at the same time. Just as the melting point is reached and decomposition begins, when the trioxide is heated, dark red fumes are given off. These can be condensed in a crystalline form.

The following series of experiments are conducted with the view of ascertaining what factors, and how they influence the volatilization of the chromium trioxide.

The material used in this series of experiments was Kahlbaum's C.P. chromium trioxide free from H_2SO_4 . Sulphuric acid, nitric acid and the halogens were tested for and none were found to be present, moisture being the only impurity which it contains. The water content was carefully determined by placing a weighed amount of the oxide in tube "CD" as shown in Fig. II, then two layers of fused Na_2CO_3 , separated from the CrO_3 by glass wool were inserted to prevent the volatilized trioxide from being carried off with the water into the weighing tube. The corks being removed, tube "CD" is placed in "L", "U" tube "C" (weighed) placed in position. "B" is closed at "X" so that the generation of gas ($O + CO_2$) in "L" will not force the bubbles of gas back through "B" instead of through the weighed tube "C". Heat is now applied to "L", the temperature gradually raised until no more gas is generated by the decomposition

Fig. 2.



of the CrO_3 , when "B" is opened at "X" and air is drawn through "E" until all of the moisture is removed, when "C" is again weighed.

"U" tube + H_2O	46.9430	21.0928 "B" + CrO_3
"U" tube	<u>46.9328</u>	<u>20.0861</u> "B" - CrO_3
H_2O	0.0102	1.0112 CrO_3

$$0.0102 \div 1.0112 = 1.00\% \text{ H}_2\text{O}$$

"U" tube + H_2O	46.9509	20.0805
"U" tube	<u>46.9399</u>	<u>19.0080</u>
H_2O	0.0110	1.0725

$$0.0110 \div 1.0725 = 1.02\% \text{ H}_2\text{O}$$

$$1. \text{ Average } 1.01\% \text{ H}_2\text{O}$$

As chromium trioxide containing a very small amount of water will evolve carbon dioxide from sodium carbonate, thus occasioning a loss of moisture, the oxide and alkaline carbonate cannot be previously mixed. Accordingly, this method of heating the trioxide and conducting the vapors through anhydrous sodium carbonate was found to be the best method of procedure.

The chromium trioxide containing 1.01% of water was heated on a platinum crucible cover, supported on a piece of heavy asbestos board, the heat being supplied by means of a Bunsen burner, and raised as fast as possible without losing CrO_3 by spitting, which will take place if oxygen is evolved too rapidly during decomposition. It has been found absolutely necessary to heat on the blast lamp to

obtain a constant weight, and also during the process of heating in all experiments to carefully protect the oxide from all reducing gases, as the CrO_3 is reduced to Cr_2O_3 without volatilization.

0.7756 CrO_3 + H_2O taken	0.7756
<u>0.2337</u> loss	<u>0.0078</u>
0.5419 Cr_2O_3 = 0.7127 CrO_3	0.7676 CrO_3 taken
0.7656 \times 1.01 = 0.0078 H_2O	<u>0.7127</u>
0.0551 \div 0.7678 = 0.0717	0.0551 loss CrO_3
\therefore 7.17% volatilized	

0.9653 CrO_3 + H_2O taken	0.9653
<u>0.2861</u> loss	<u>0.0097</u>
0.6792 Cr_2O_3 = 0.8933 CrO_3	0.9556 CrO_3 taken
0.9653 \times 1.01 = 0.0097 H_2O	<u>0.8933</u>
0.0623 \div 0.9556 = 0.0652	0.0623 loss CrO_3
\therefore 6.52% volatilized.	

In a second series of experiments chromium trioxide which had been dried in an air bath for eight hours at a temperature of 125° , was used. The amount of water in this sample was determined in the same way as above, and found to be .45%.

"U" tube + H_2O	31.5474	48.9007
"U" tube	<u>29.6469</u>	<u>48.8911</u>
H_2O	1.9005	0.0096

$$0.0096 \div 1.9005 = .50\% \text{ H}_2\text{O}$$

"U" tube + H ₂ O	48.9004	29.6489
"U" tube	<u>48.8944</u>	<u>28.3634</u>
H ₂ O	0.0050	1.2855
0.0050 - 1.2855 = .39% H ₂ O		
2 Average .45% "		

The amount volatilized is then determined on this sample in the usual manner.

1.1188 CrO ₃ + H ₂ O taken	1.1188 CrO ₃ + H ₂ O
<u>0.3293</u> loss	<u>0.0050</u> H ₂ O
0.7895 Cr ₂ O ₃ = 1.0384 CrO ₃	1.1138 CrO ₃ taken
1.1188 X .45 = .0050 H ₂ O	<u>1.0384</u>
0.0754 ÷ 1.1138 = 0.0677	0.0754 loss CrO ₃
6.77% volatilized	

1.2020 CrO ₃ + H ₂ O taken	1.2020 CrO ₃ + H ₂ O
<u>0.3479</u> loss	<u>0.0054</u> H ₂ O
0.8541 Cr ₂ O ₃ = 1.1233 CrO ₃	1.1966 CrO ₃ taken
1.2020 X .45 = 0.0054 H ₂ O	<u>1.1233</u>
0.0733 ÷ 1.1966 = 0.0612	0.0733 loss CrO ₃
6.12% volatilized	

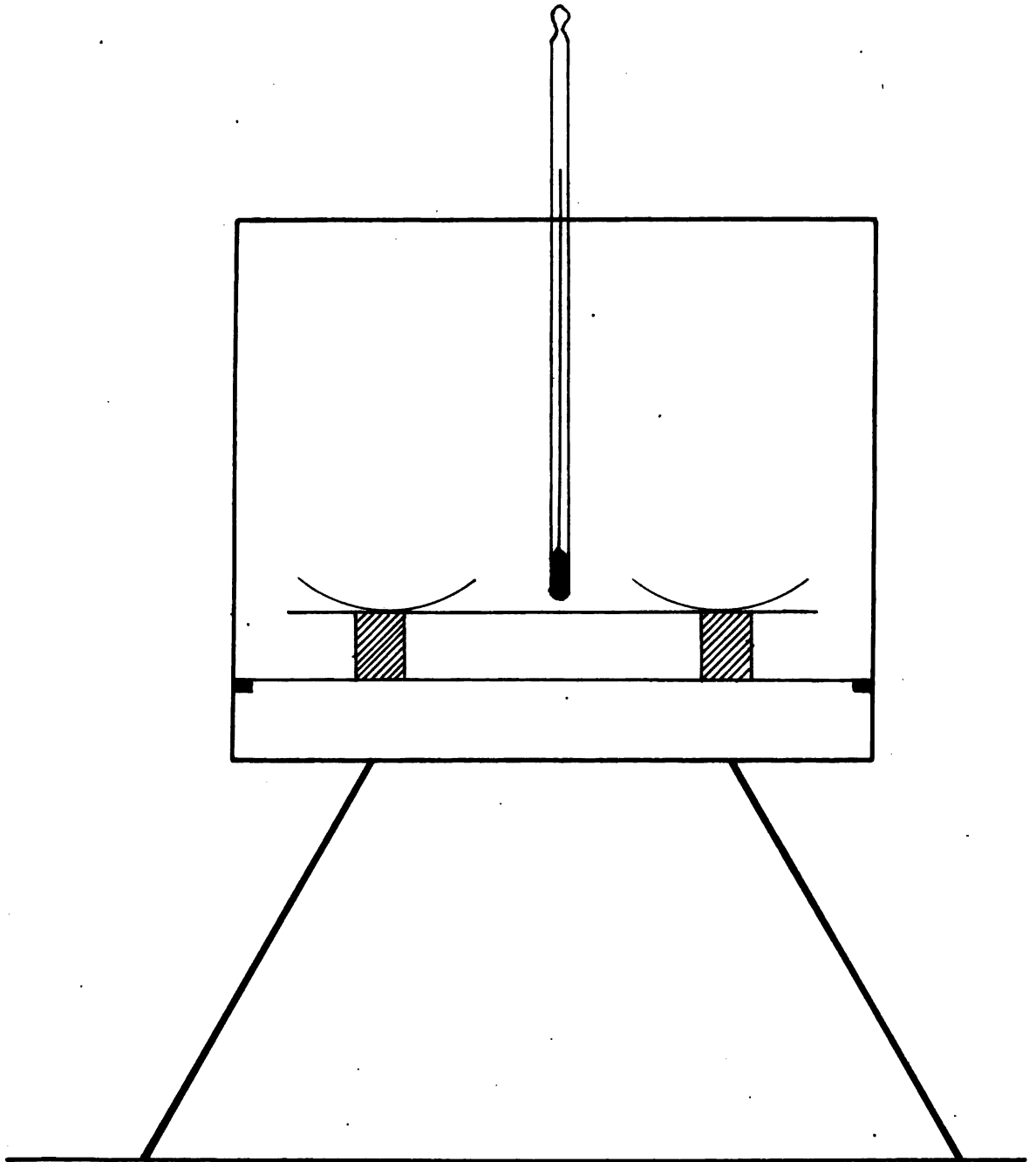
In a third series of experiments the trioxide was first fused, the water content determined on five grams of the oxide, which had been fused at the lowest possible temperature and the material was found to be anhydrous. The fused oxide is now volatilized in the usual manner.

Wt. CrO_3	Loss ($\text{O} + \text{CrO}_3$)	% CrO_3 volatilized
.6705	.1977	7.27

From these results it is evident that, other conditions being the same, small amounts of water have no influence on the volatility of the oxide. As a matter of fact the red vapor is given off only after a state of fusion has been reached, and at this time the oxide is anhydrous. That CrO_3 retains traces of water tenaciously at temperatures below its melting point, is evident from the fact that an experiment was conducted in which the oxide containing 1.01% water was heated in vacuo for 20 hours at 150° , phosphorus pentoxide being present in the vessel at the same time. After this treatment traces of water were found to be present in the oxide.

As to the effect of temperature on the volatilization of the oxide, it is seen that volatilization begins just above the melting point, and increases rapidly for the few first degrees, but soon reaches a point where it goes very slowly. This point is marked by the solidification of the fused CrO_3 in consequence of loss of oxygen. Immediately above this point, not much CrO_3 is volatilized, but at a higher temperature approaching a dull red heat, volatilization occurs rapidly and quite completely; the last of the trioxide being driven off only at a bright red heat. The rate at which the temperature is raised, providing it is raised high enough to cause complete decomposition, makes

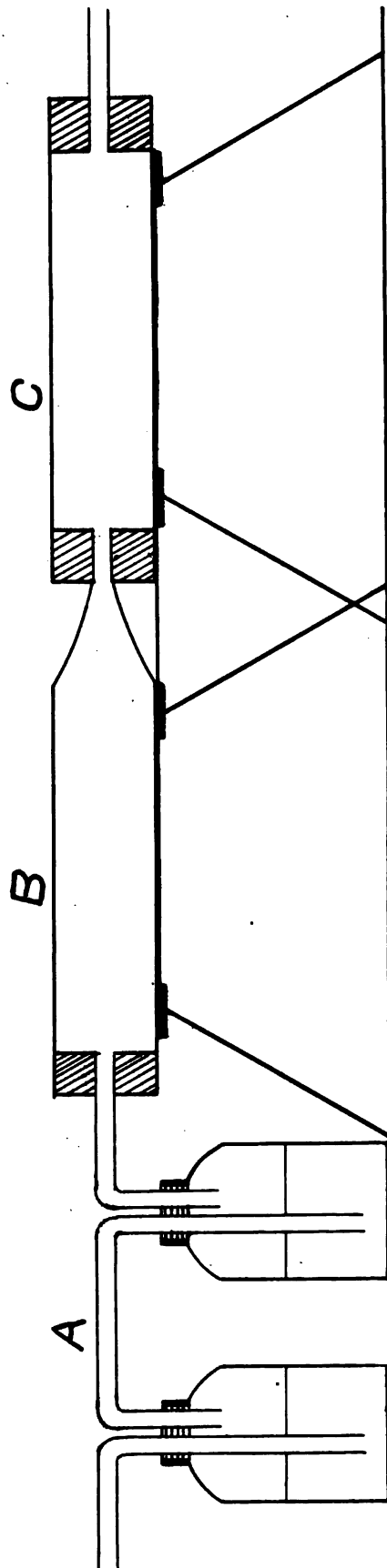
Fig. 3.



no difference in the per cent volatilized. At temperatures near the decomposition point it is possible to get CrO_3 to a constant weight, only after prolonged heating, and for small changes in temperature there is a marked difference in the weight lost. Two samples of the CrO_3 containing 1.01% water were placed on small weighed watch glasses and heated in an air bath (Fig. III) for 70 - 80 hours at $220^\circ - 230^\circ$ when a constant weight was obtained with a loss of 13.9%, and 14.2%. Another set of samples from the same lot of CrO_3 was heated under the same conditions as before at a temperature of $230^\circ - 240^\circ$ until a constant weight was reached, when 20.3% and 20.87% was found to have been lost.

As the foregoing experiments were being carried out, indications seemed to point to the fact that the greater the surface of the oxide exposed, the greater the amount of volatilization. In order to offer greater surface during the process of volatilization, the trioxide was heated, and a portion of the volatilized oxide was condensed on weighed asbestos fibre or glass wool. The CrO_3 to be volatilized is placed in a glass tube "B" (Fig. 4.) where it is heated by means of a Bunsen burner. During the heating a stream of dry air is drawn over the oxide in the tube "B", through wash bottles "A", containing H_2SO_4 . This dry air carries the fumes of the trioxide through the narrowed neck of "B", into weighed tube "C", containing the glass wool. The CrO_3 is then revolatilized by removing the glass wool and trioxide from

Fig. 4.



the tube and heating in a porcelain dish.

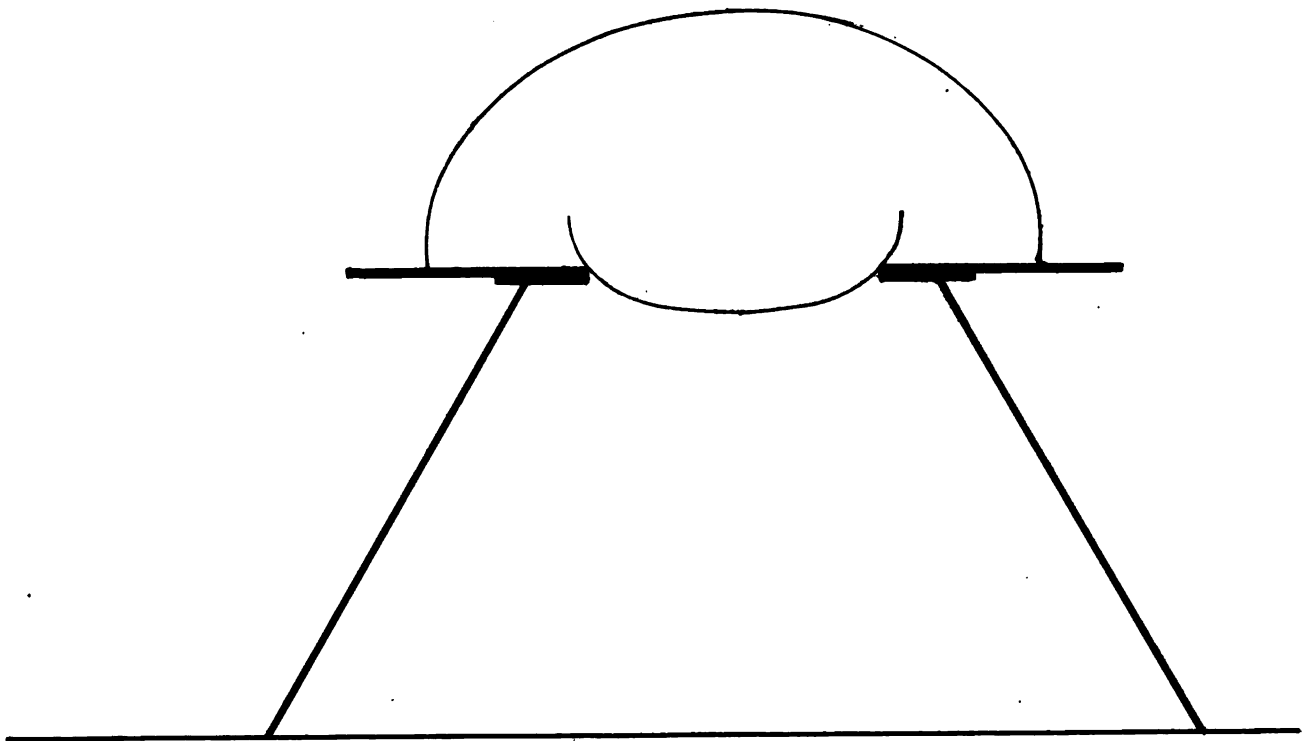
Wt. CrO_3	Loss ($\text{CrO}_3 + \text{O}$)	% CrO_3 volatilized
.1951	.0641	11.68
.1221	.0551	27.02
.1007	.0352	13.51

In these experiments, as well as in those conducted in a similar manner with asbestos fibre, as the vapor arises it appears to be more or less condensed by the upper layers of the fibre or glass wool, yet by this means, the per cent of the trioxide volatilized is greatly increased, especially if not too thick a layer of glass wool or fibre is used.

In the following series of experiments the oxide was placed in a porcelain dish resting on a piece of asbestos board (Fig. 5), from which it was volatilized and collected on a weighed platinum dish inverted over the porcelain dish. By this means the oxide was spread over the large surface of the platinum dish, from which it could be directly volatilized without any opportunity for condensation due to glass wool or fibre. These last experiments gave by far the greatest amount of volatilization observed.

Wt. CrO_3	Loss ($\text{CrO}_3 + \text{O}$)	% CrO_3 volatilized
.0216	.0193	65.85
.0193	.0154	73.59
.0239	.0171	62.75
.0125	.0085	57.60
.0317	.0240	68.14

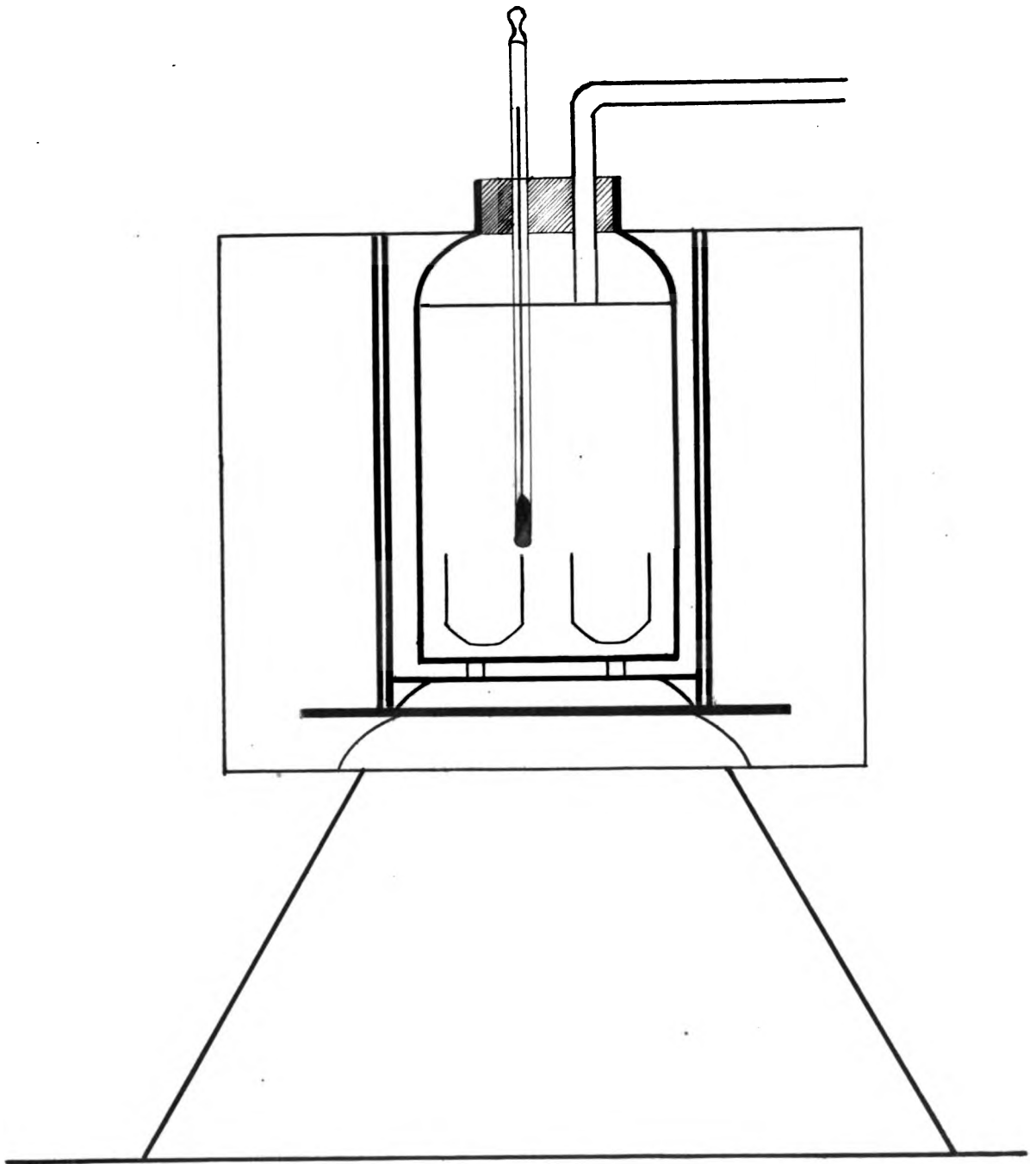
Fig.5.



Wt. CrO_3	Loss ($\text{CrO}_3 + \text{O}$)	% CrO_3 volatilized
.0217	.0140	53.46
.0213	.0172	72.02

Considerable diminution in pressure has but little influence on the volatility of the CrO_3 . Two grams of the chromium trioxide which had been carefully rendered anhydrous by fusion, were heated in an air bath (Fig. VI) under a pressure of 26 mm. and showed no loss in weight, but remained apparently unchanged. No sublimate could be detected in the bottle in which the experiment was conducted. This same experiment was conducted in an apparatus similar to that used by Actowski, but it was found impossible to obtain any signs of the crystals mentioned by him. Two grams of the fused oxide were heated under the same conditions of pressure, but with the temperature raised so that it stood from 185° to 198° for a period of 14 hours, and again there was no change in weight or appearance. Two fresh samples were heated under a pressure of 26 mm. at 200° for 14 hours with a loss of .39% and .33% respectively. At this point volatilization of the oxide had just begun, as was indicated by a slight coating which appeared on the thermometer and sides of the porcelain crucible containing the trioxide. Duplicate samples were heated in the same apparatus at 130° to 140° and up to 185° to 190° under atmospheric pressure without any change. When the temperature

Fig. 6.



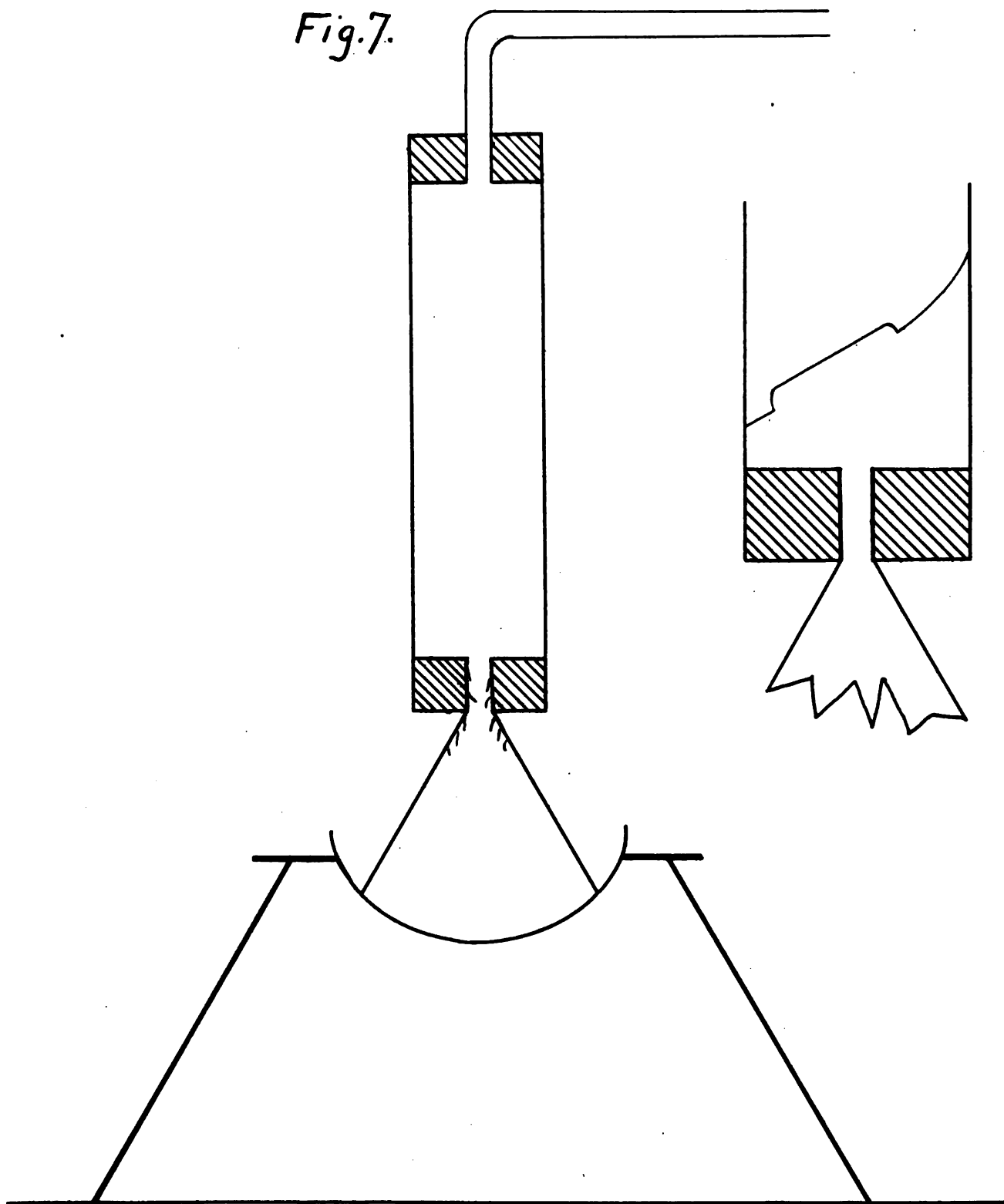
is raised to the neighborhood of 200° under atmospheric pressure, CrO_3 begins to volatilize in small quantities, as can be seen by the coating on the sides of the crucible.

From these experiments it is obvious that by decreasing the pressure to 26 mm., the volatilization is not apparently increased, nor on the other hand does increase in pressure seem to have any influence on the volatility of the oxide.

Notwithstanding that analysis has failed to reveal the presence of impurities other than water, the oxide was sublimed and when subjected to analysis showed itself to be CrO_3 . This was accomplished by fusing some CrO_3 containing 1.01% of water in a hard glass test tube. Above the fused oxide was placed a thick layer of glass wool, and covering the top of the crucible was a weighed platinum crucible cover on which the volatilized oxide is condensed.

In order to determine if it were possible to condense a more volatile portion of the oxide, a series of sublimations were carried on as follows: About 4 kilos of the trioxide were heated, small portions at a time in a porcelain evaporating dish (Fig. VII), supported on a piece of asbestos board. The fumes were drawn through an inverted funnel by means of a current of air, into a large tube containing glass wool. The glass wool on which the CrO_3 was deposited is removed from the tube, and placed in the evaporating dish from which the original trioxide was

Fig.7.



sublimed, heated as before and collected on a fresh lot of glass wool. This condensation and sublimation was repeated four times. Small portions were taken from each fraction, by condensing a portion of the sublimed oxide on a platinum crucible cover as shown in Fig. VII and tested as to their volatility.

Second Fraction.

CrO ₃ taken	Loss (CrO ₃ + O)	% CrO ₃ volatilized
.1342	.0641	31.30
.1800	.0828	29.00

Third Fraction.

.0218	.0091	23.39
.0250	.0105	23.60

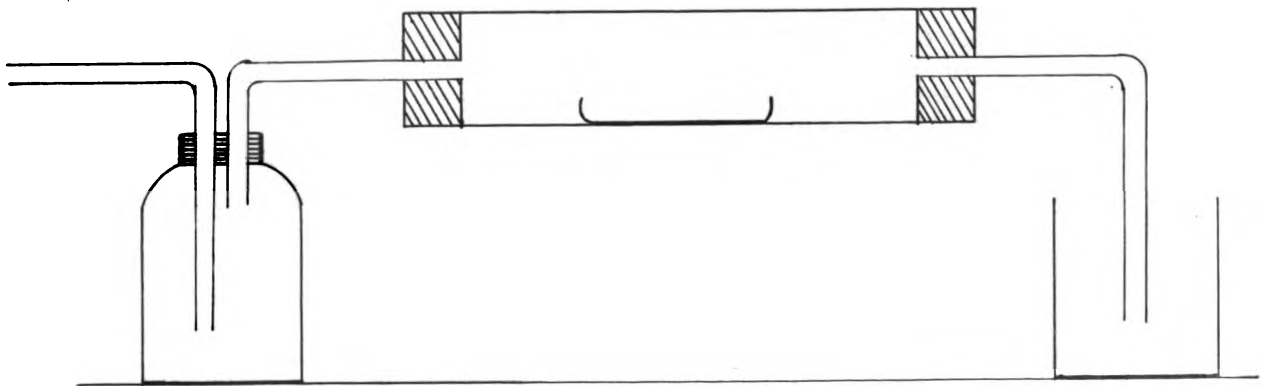
Fourth Fraction.

.0093	.0039	23.65
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The chromium trioxide caught on the glass wool was examined under the microscope, and in all cases found to be condensed in a crystalline form. Large crystals 1/8 of an inch long are often formed in the neck of the funnel.

A final series of experiments were conducted to ascertain the effect of the presence or absence of oxygen on the amount of oxide volatilized. In these experiments the oxide was placed in a porcelain boat and heated in a hard glass tube through which a current of the gas was passing (Fig. VIII), no attempt being made to secure a

Fig. 8.



• large surface.

Wt. CrO_3	Loss ($\text{CrO}_3 + \text{O}$)	% CrO_3 volatilized
.3107	.0829	3.54
.3426	.0866	<u>1.72</u>
Mean		2.63

In a second series of experiments carbon dioxide was substituted for oxygen with similar results.

Wt. CrO_2	Loss ($\text{CrO}_3 + \text{O}$)	% CrO_3 volatilized
.2185	.0560	2.19
.2374	.0644	<u>4.17</u>
Mean		3.18

When these results are compared with those obtained under similar conditions, but in a current of air, it appears that the gaseous atmosphere has no influence on the volatility of the oxide.

From the above series of experiments made under varying conditions, it appears that chromium trioxide is slightly volatile at temperatures just above its melting point and not at all below. While only a small percentage of the oxide can be volatilized under ordinary conditions, the amount which can be volatilized from a given quantity can be increased by increasing the surface of the oxide exposed. The factors of increased, or diminished pressure, or the influence on non-reducing gases has apparently very little effect on this volatility. Further this volatilization begins just above the melting point of the oxide, 193° and

vapors continue to appear until a red heat is reached when decomposition into the sesquioxide and oxygen is complete.

Approved Victor Lenher May 19, 1905

W. W. Daniels C. K. Leith

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